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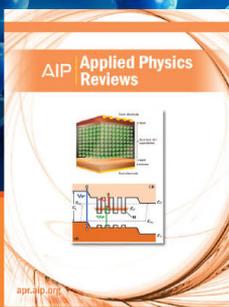
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Electronic structure of small GaAs clusters

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The electronic structure of small Ga_xAs_y clusters ($x + y < 10$) are calculated using the local density method. The calculation shows that even-numbered clusters tend to be singlets, as opposed to odd-numbered clusters which are open shell systems. This is in agreement with the experimental observations of even/odd alternations of the electron affinity and ionization potential. In the larger clusters, the atoms prefer an alternating bond arrangement; charge transfers are observed from Ga sites to As sites. This observation is also in agreement with recent chemisorption studies of ammonia on GaAs clusters. The close agreement between theoretical calculations and experimental results, together with the rich variation of electronic properties of GaAs clusters with composition makes GaAs clusters an ideal prototype system for the study of how electronic structure influences chemical reactivity.

I. INTRODUCTION

The understanding of the relationship between the geometrical and the electronic structure of a solid surface is of crucial importance for the understanding of many of its physical and chemical properties. In particular, it is known from chemisorption studies on metal and semiconductor surfaces that certain sites on the surface as well as facets can be much more reactive than others.¹ These effects are caused by the fact that the local electronic structure of a surface can be very sensitive to the position of neighboring atoms.

Cluster science offers a particularly interesting area in which the correlation between reactivity and structure can be investigated. In a small cluster, the concentration of surface atoms is enhanced relative to bulk atoms. In addition, the surface of a small cluster provides several different chemisorption sites. The relative concentration of such sites is naturally much larger than what would be the case on, for example, a stepped surface.

Several recent experiments probing the sticking coefficient of simple molecules such as H_2 and NH_3 on small clusters have shown that the reactivity of a cluster can depend very sensitively on the cluster size.²⁻⁵ In addition, it has been shown that for a given composition of a cluster, there can exist several different isomers each of which can have a very different reactivity.

These types of experiments cannot be properly interpreted without detailed knowledge of the electronic and geometrical structure of the cluster. At present, such information can best be provided by theoretical calculations.

The exact numerical calculation of the electronic structure of molecules larger than dimers would be prohibitively time consuming even with present supercomputers. One must therefore develop some approximate schemes. Among the first principles approximations one can distinguish configuration interaction theory (CI) and density functional theory (DF). The two theories are formally exact but by restricting the number of configurations or choosing simplified exchange correlation functionals practical approximate computational schemes result.

To date, most applications to solids, molecules, and atoms have shown that the different density functional approaches provide almost the same accuracy as CI but with a tremendous reduction in computational effort.

In the present paper detailed calculations of the electronic structure of small GaAs clusters will be presented and compared to recent experimental data.

The theoretical calculations are performed using the local density approximation (LDA). By minimizing the total energy, the equilibrium structure is obtained and the electronic structure calculated. The computational method, DMol⁶ is briefly described in Sec. II.

In Sec. III A an application to Ga_xAs_y dimers is presented. For such small systems, conventional quantum chemistry methods such as the multiple CI theory can be applied. It is shown that the present LDA approach is as accurate as other high level methods.

In Sec. III B the electronic structure and equilibrium geometry of various Ga_xAs_y clusters of size range from $x + y = 3-10$ is presented. The emphasis is on the near $x = y$ composition, which is the dominant composition observed in experiments.⁷

In Sec. IV, the calculations are compared with recent experimental results. It is shown that even-numbered clusters have singlet electronic states and that the odd-numbered clusters are triplets. In the larger clusters, the atoms prefer an alternating bond arrangement where charges are transferred from the gallium atoms to the adjacent arsenic atoms.

II. THEORY

In this section, some theoretical details will be presented. In the first subsection, the local density approximation is discussed. In the second subsection, the numerical methods and procedure will be briefly introduced.

A. Theoretical formalism

Since its introduction,^{8,9} The density functional theory has emerged as an extremely efficient method for the first

principles calculation of the electronic structure of many-electron systems.¹⁰ Density functional theory is a formally exact method for the reduction of a complicated many-electron problem to a set of interacting one-electron equations. For a general many-electron problem the total energy and the electronic density in the system can be obtained by the solution of the following set of one-electron problems:

$$[-\nabla^2 + V_s(\mathbf{r}) + \mu_{xc,\sigma}(\mathbf{r})]\psi_{k,\sigma}(\mathbf{r}) = \epsilon_{k,\sigma}\psi_{k,\sigma}(\mathbf{r}). \quad (2.1)$$

In this equation, $V_s(\mathbf{r})$ is the electrostatic potential at position \mathbf{r} . The spin is denoted by σ . The effects of exchange and correlation is taken into account through the exchange correlation potential $\mu_{xc,\sigma}(\mathbf{r})$ which is a functional of the electronic density $\rho_\sigma(\mathbf{r})$ in the system. The electron density can be obtained from

$$\rho_\sigma(\mathbf{r}) = \sum_{\text{occ}} |\psi_{k,\sigma}(\mathbf{r})|^2, \quad (2.2)$$

where the sum is over the lowest occupied states. In most practical applications one performs the local density approximation, i.e., one approximates μ with the exchange correlation contribution for a homogeneous electron gas of density $\rho(\mathbf{r})$. This approximation is obviously valid for slowly varying electron density systems. Applications have shown that even such inhomogeneous systems as atoms can be well described by the LDA.

Once the electron density distribution is calculated, the total energy can be obtained from

$$E^{\text{tot}} = \sum_{\text{occ}} \epsilon_{k,\sigma} + \sum_{\sigma} \int d\mathbf{r} \rho_{\sigma} [\epsilon_{xc,\sigma} - \mu_{xc,\sigma} - \frac{1}{2} V_e] + E^{\text{nuc1}}, \quad (2.3)$$

where E^{nuc1} is the repulsion between the nuclei in the system and V_e is the electrostatic potential due to the electron charge distribution. In this equation $d(\rho_{\sigma}\epsilon_{xc,\sigma})/d\rho_{\sigma} = \mu_{xc,\sigma}$. In the present application, an approximation for the exchange correlation potential derived by Hedin and Lundqvist¹¹ is used.

B. Computational details

The linear variational expansion of the single-particle molecular orbital

$$\psi_{k,\sigma}(\mathbf{r}) = \sum_{k,\sigma} c_{k,\sigma}^j \phi_j(\mathbf{r}) \quad (2.4)$$

is used to solve Eq. (2.1). Here ϕ_j are atomic orbitals centered at each nucleus and c^j are the expansion coefficients. In the present work, accurate numerical atomic orbitals are used and integrations of the Hamiltonian matrix elements are made numerically. The Schrödinger equation is solved self-consistently on a set of discrete sampling points surrounding the molecule.

In DMol the grid is generated spherically around each nucleus (as atomic center) with increasing radial spacing. The spherical shells around different nuclei penetrate each other and no boundary faces are introduced. Gaussian quadrature rules are applied to the integrations over the spherical

shells. In order to compensate the possible “double counting,” the integration weight on a grid node is split if the same spatial region is also sampled by another spherical shell of grid. By splitting the weights the grid is decomposed into each atomic center.

For each decomposed, spherical grid, the central region is densely sampled and the regions near the neighboring nuclei are relatively scarcely sampled. To eliminate the singular effects due to the nuclear cusp at an off-center nucleus, the weight is reduced for the grid nodes near this off-center nucleus. Meanwhile, this same region is also sampled by the spherical grid attached to that off-center nucleus with nearly fully weighed nodes. The proper splitting of the weights insures integrations over each decomposed grid to be precise. Details of this partitioning technique are given by Becke¹² and Delley.⁶

The partitioning of the molecular grid into atomic centers makes it convenient to use a multipolar expansion technique to facilitate the convergence of the SCF iterations.⁶ The multipolar components of the charge density ρ may be expressed as

$$\rho_{\alpha,l,m}(s) = \int_{s=|\mathbf{r}-\mathbf{R}_{\alpha}|} p_{\alpha}(\mathbf{r})\rho(\mathbf{r})Y_{l,m}(\mathbf{r}-\mathbf{R}_{\alpha})d\Omega, \quad (2.5)$$

where $Y_{l,m}$ is a spherical harmonic function of angular dependence (l,m) , \mathbf{R}_{α} is the position of the α th atomic center. The partitioning function p_{α} satisfies the requirements $\sum_{\alpha} p_{\alpha}(\mathbf{r}) = 1$ at every point \mathbf{r} . The integration is over the spherical shells centered at \mathbf{R}_{α} .

Since the off-center contribution to the charge density at a point \mathbf{r} is effectively eliminated by the partitioning function $p_{\alpha}(\mathbf{r})$, the product $p_{\alpha}(\mathbf{r})\rho(\mathbf{r})$ is nearly spherically symmetric. The multipolar expansion of this decomposed charge density is expected to converge rapidly. Practically a maximum angular momentum of 2 or 3 provides good accuracy in our applications.

The Coulomb potential is treated in a similar way, i.e., first partitioned into individual atomic centers and then expanded in terms of spherical harmonics. The multipolar components of the Coulomb potential are related to the multipolar components of the charge density via the Green's function defined by the Poisson's equation. The use of a multipolar expansion technique greatly simplifies the evaluation of the Coulomb potential which is normally a multicenter integration.

In DMol, atomic orbitals that are exact numerical solutions of a neutral atomic systems are used as the basis functions. The use of such basis functions significantly reduce the size of the basis compared to Gaussian methods. For a molecule these basis functions fit naturally to the charge distribution in the regions near the nuclei and predict the right decomposition limit at infinite internuclear distances. To describe the intermediate regions, extended basis functions from positively charged atomic systems are added.

III. RESULTS

In this section, results for the electronic structures of Ga_xAs_y clusters are presented. In the first part, the numeri-

cal accuracy of the density functional approach is shown by an application to dimers and comparison with the experiment and other high level quantum chemistry methods. In the second part, application of the present method is extended to clusters of larger size. All the computations included in this work are accomplished on a Silicon Graphics personal computer.

A. Gallium arsenide dimers

The accuracy of a molecular calculation depends on the quality of the basis set.

In the present work, two numerical basis sets are used. The first set includes all the occupied atomic orbitals of free Ga and As atoms and one additional function (from ionic Ga and As) for each of the $3d$, $4s$, and $4p$ orbitals, plus a $4d$ orbital as polarization function. This basis set is denoted DNP. The second set is obtained from the DNP by removing the extended $3d$ and $4d$ functions and freezing the core orbitals. This reduced basis set is denoted dn . The DNP set is used only for diatomic calculations. In the calculations for the clusters with 3 to 10 atoms (presented in the next subsection), the reduced set dn is used.

In Table I, DMol's results for the gallium arsenide dimers are presented and compared with experiment and multiple CI calculations. We can see that the DNP set gives very accurate results for the equilibrium distance and vibrational frequency. For the reduced set, as a consequence of freezing the core orbitals, the bond lengths are increased by a few percent and the binding energy is decreased. In general, however, this reduced basis set gives a fairly good picture of the GaAs dimers.

The potential energy curves for the dimers As_2 , GaAs, and Ga_2 are presented in Figs. 1(a)–1(c). The solid curves are obtained with the basis set DNP and the dashed curves

are obtained with the basis set dn . The As_2 dimer is a singlet with a HOMO–LUMO gap of about 2 eV at its equilibrium separation 2.1 Å. It can be seen that the potential energy curve for As_2 [Fig. 1(a)] is relatively deep near the equilibrium distance. The other two dimers, GaAs and Ga_2 , are triplets, each is shown with the energy curves of the two lowest-lying states as indicated in Figs. 1(b) and 1(c). These curves are relatively flat compared with As_2 (different energy scales are used to avoid confusion). The Ga_2 curves extend further to the right.

B. Small gallium arsenide clusters

The number of possible atomic arrangements of a cluster increases rapidly with cluster size. In order to systemize the search for the equilibrium structures of the different GaAs clusters, possible initial configurations must be defined as seeds for the LDA calculation and energy optimization. In the present case we started by considering clusters of stoichiometric composition, i.e., Ga_xAs_x . Recent UPS data¹³ suggests that these clusters are of closed shell type.

The search began by defining possible geometries using Polya theory of counting¹⁴ and the geometries previously optimized for silicon clusters.^{15–18} For simplicity, all the bond lengths were fixed to the GaAs bulk values. This procedure defines several hundred different structures.

The electronic structure of these configurations were calculated using an extended Huckel method (EHT). Those geometries that came out as closed shell structures were first selected as seeds for geometry optimization. Comparisons of the EHT band structure with the LDA results for a given cluster geometry indeed show a very good qualitative agreement. In addition to these configurations we used a large number of open shell configurations as seeds. The seeds for the nonstoichiometric clusters were defined by substituting

TABLE I. Results for dimers GaAs, As_2 , and Ga_2 . R_e is the equilibrium separation. E_b is the binding energy defined as the difference between the molecular energy and the sum of atomic energies, and ω is the vibrational frequency. IP stands for ionization potential and EA for electron affinity.

Dimers	R_e (Å)	E_b (eV)	ω_e (cm ⁻¹)	IP (eV)	EA (eV)	References
GaAs(³Σ⁻)						
Expt.					2.1	13
Expt.	2.53 ± 0.02	2.06 ± 0.05	215	7.2 ± 0.8		22
LDF(DNP)	2.549	2.50	209	7.8	1.82	Present work
LDF(dn)	2.65	2.16		7.8	1.89	Present work
CCSD	2.588		210			23
FOCI	2.645	1.24	187	5.19	0.89	20
SOCI	2.60		215	1.3		20
MRDCI	2.60	1.4	202	6.94		24
As₂(¹Σ⁺)						
Expt.	2.103	3.96	430	9.9		25
LDF(DNP)	2.110	4.77	427	10.3	0.63	Present work
LDF(dn)	2.180	3.88		10.6	0.96	Present work
SCF	2.059		514	8.7	0.42	26
CCSD	2.107		447	9.8	0.59	26
MCSCF	2.164	2.71	394			27
Ga₂(³Π_u)						
LDF(DNP)	2.716	1.74		6.6	1.6	Present work
SCF	2.762		162			23
CCSD	2.715		169			23
CASSCF	2.762		158			28

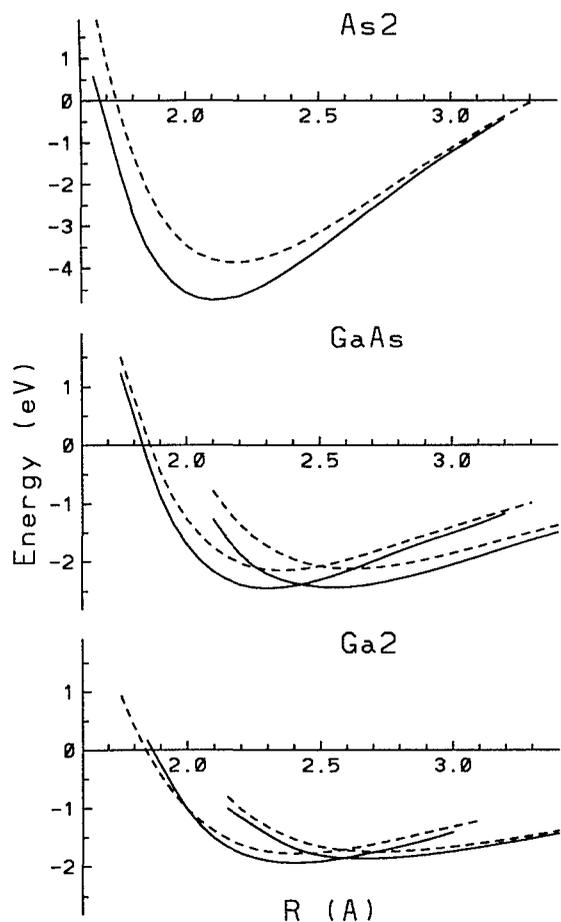


FIG. 1. Potential energy curves of diatomic molecules (a) As_2 (${}^1\Sigma_g^-$), (b) GaAs (${}^3\Sigma^-$ to the left and ${}^3\Pi$ to the right), and (c) Ga_2 (${}^3\Sigma^-$ to the left and ${}^3\Pi$ to the right). The result of the basis set DNP is plotted in solid lines and the result of the basis set dn is plotted in dashed lines. See the text for details.

and removing various atoms of the stoichiometric clusters.

The different seed configurations were relaxed by DMol to find the local energy minima. The reduced basis set was used in this procedure. During the relaxation, the bond lengths and charge transfer changed about 5–30% and the total energy typically decreased a few tenths of an electron volt per atom. The geometry relaxation ended when the

maximum energy gradient was smaller than 0.003 a.u. Only low order nondegenerate point groups were used to restrict the degrees of freedom in the geometrical relaxation.

The equilibrium configuration of each cluster is chosen as the structure with the deepest local minimum. In view of the large number of initial structures, we feel confident that the configurations obtained lie very close to the true equilibrium geometries.

The binding energy, HOMO energy, band gap, and vertical EA and IP of the gallium arsenide clusters in their relaxed configurations are listed in Table II.

Clusters of $(x + y) = 4, 6, 8,$ and 10 atoms are of closed shell singlet ground states and all, except for Ga_4As_4 , have band gaps larger than 1 eV at the lowest energy configuration. There is an apparent even/odd oscillation in electron affinity. The EA of Ga_4As_4 is 2.8 eV, larger than expected from the oscillation trend but consistent with the relatively small band gap of 0.4 eV. More details about this cluster will be presented later.

There is no clear division between IP's of even- and odd-numbered clusters. These IP's are all calculated vertically on the relaxed configurations of neutral clusters; no geometry optimization is made for the positively charged clusters in the present work.

The structures we found the most stable for the gallium arsenide clusters are schematically plotted in Figs. 2(a)–2(j). We can see that these structures are close in shape to certain polyhedra. In particular, some polyhedral structures found stable for the silicon clusters were also found stable for the gallium arsenide clusters of the same size in our calculations.

A typical example is Ga_5As_5 . The lowest energy structure found for this isomer is a tetracapped trigonal prism (TTP), see Fig. 2(i), formed by decorating Ga atoms on the faces of a distorted trigonal prism with atoms on the vertices. By substitution of the atoms in the adjacent vertices, another configuration of nearly equal energy was found. The TTP structure was previously found to be the most stable for the Si_{10} cluster in the SA-LDA calculation.¹⁵

The tetracapped octahedral (TO) structure [Fig. 2(j)] which was found to be almost equally stable for the Si_{10} cluster¹⁸ also resulted in a high binding energy for the Ga_5As_5 cluster. A couple of different atomic arrangements with sim-

TABLE II. Results for the gallium arsenide clusters in the most stable structure. The geometry of each cluster is represented by a polyhedron. The symmetry each structure processes is indicated. Δ is the HOMO-LUMO separation. For open shell systems the values of Δ are in parentheses. The units are eV/atom for binding energy E_b , and eV for the others.

$x + y$	Ga_xAs_y	Configurations	ptgrp	E_b	HOMO	Δ	IP	EA
10	Ga_5As_5	Tetracapped trigonal prism	C_s	2.65	6.0	1.7	8.0	2.4
9	Ga_4As_5	Tricapped trigonal prism	C_s	2.54	5.6	(0.2)	7.5	3.5
8	Ga_4As_4	Rhombic prism	C_i	2.54	5.1	0.4	7.3	2.8
7	Ga_3As_4	Capped prism	C_s	2.43	5.1	(0.3)	7.2	2.9
6	Ga_3As_3	Capped trigonal bipyramid	C_1	2.43	5.7	2.0	8.0	1.6
5	Ga_2As_3	Trigonal bipyramid	C_{2v}	2.40	5.6	(0.6)	8.0	2.7
4	Ga_2As_2	Planar rhombus	D_{2h}	2.22	5.6	1.2	8.0	1.8
3	Ga_1As_2	Triangle	C_{2v}	1.93	5.3	(0.5)	8.1	2.1
2	GaAs	Linear	C_{2v}	1.08	4.8	(0.2)	7.8	1.9

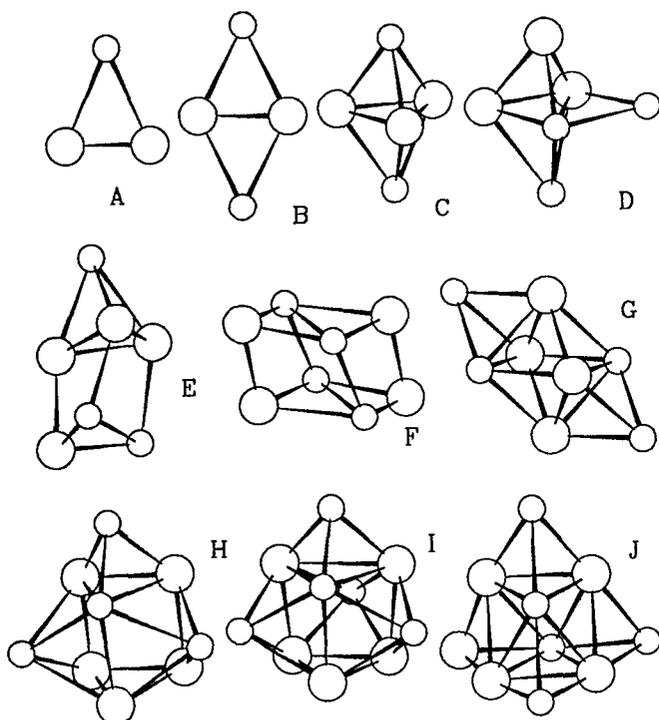


FIG. 2. Geometry of the most stable $Ga_x As_y$ isomers with near $x = y$ composition. The bigger circles represent As atoms and the smaller circles represent Ga atoms. Sticks are added between the balls intended to help for a three-dimensional perception, which do not necessarily represent a bond of any sort. The detailed geometries will be provided upon request. (a) $GaAs_2$, isosceles triangle; (b) Ga_2As_2 , planar rhombus; (c) Ga_2As_3 , trigonal bipyramid; (d) Ga_3As_3 , edge capped trigonal prism; (e) Ga_3As_4 , capped trigonal prism; (f) Ga_4As_4 , rhombic prism; (g) Ga_4As_4 , bicapped octahedron; (h) Ga_4As_5 , TTP; (i) Ga_5As_5 , tetracapped trigonal prism (TTP); (j) Ga_5As_5 , tetracapped octahedron (TO).

ilar energies were found for this type of structure.

In these structures the outer atomic sites are occupied by gallium; a Mulliken population analysis shows that these atomic sites are substantially positively charged. Experiments have revealed three or four active reaction sites on the Ga_3As_5 isomer. The number of positively charged sites in our calculations agrees well with this finding. It is natural to suppose that these positively charged sites are surrounded by negatively charged sites for charge conservation and energetic stability. This suggests an alternating pattern for the arrangements of the two types of atoms. A recent simulated annealing local density approximation (SA-LDA) calculation of this isomer also suggested an alternating arrangement.¹⁹

Similar alternating atomic arrangements are found for the other clusters $Ga_x As_y$ with nearly equal number of Ga and As atoms. Not a single configuration was found in our calculations (for $x + y > 3$) where it was energetically favored for the nearest neighbors of an atom to be of the same species. Several seed configurations were tested with the two species segregated. These segregated arrangements were found less stable (by 0.5–1.0 eV than the lowest energy structure of the same isomer).

The TTP and TO are particularly stable structures—the binding energy per atom is about 2.6 eV. It is reasonable to expect that the adjacent odd-numbered clusters have similar

configurations. The search for energy minima of the Ga_4As_5 isomer started with the seeds obtained by removing one capping Ga atoms from the TTP or TO structures of the Ga_5As_5 isomer. The binding energies of the relaxed structures are about 2.5 eV. The most stable one is a distorted TTP [Fig. 2(h)].

The lowest energy structure for the Ga_4As_4 isomer is a rhombic prism with C_i symmetry [Fig. 2(f)]. This structure is 0.14 eV/atom more stable than the bicapped octahedral structure [Fig. 2(g)], previously found to be the most stable for Si_8 .

In this structure, the As atoms are located outside of the Ga atoms. This is an exception in the general trend observed in our results. The structure was obtained by relaxing a bicapped octahedral structure with two As atoms in the capped positions. For this seed geometry, the relaxation took an unusually long time (over 200 h) but finally the rhombic structure resulted. The efforts for different substitutions of atoms failed to reach a structure of comparably low energy.

Another point worth mentioning is that all the seed configurations we have tried for this isomer ended up with a band gap less than 1 eV, which is clearly smaller than that of the adjacent even-numbered isomers, Ga_5As_5 and Ga_3As_3 , see Table III. Note that the trigonal antiprism structure for Ga_4As_4 listed in this table has a segregated arrangement of Ga and As atoms.

For the Ga_4As_4 , the cubic structure with an alternating arrangement is unstable due to the static Jahn–Teller effects. The distorted descendants with lower order symmetry (e.g., C_{2v}) are still not energetically favored.

The lowest energy structure for the Ga_3As_4 isomer was obtained by relaxing a capped trigonal prism as the seed configuration. See Fig. 2(e).

The lowest energy structure for Ga_3As_3 was obtained by relaxing an edge capped trigonal prism [Fig. 2(d)], which is also the most stable structure for the Si_6 cluster.¹⁸ The (distorted) octahedral structures are less stable.

The lowest energy structure for the Ga_2As_3 isomer was obtained by relaxing a trigonal bipyramid [Fig. 2(c)]. A similar structure was previously found stable for Si_5 .¹⁶

The most stable structure for Ga_2As_2 was a planar rhombus in D_{2h} symmetry [Fig. 2(b)]. The rhombic structure we found agrees well in bond lengths and bond angles

TABLE III. Results for some even-numbered gallium arsenide clusters in different atomic arrangements. The units are eV/atom for the binding energy E_b and eV for others. See captions for Table II.

$Ga_x As_y$	Configurations	ptgrp	E_b	HOMO	Δ
Ga_5As_5	Tetracapped trigonal prism	C_s	2.65	6.0	1.7
	Tetracapped octahedron	C_i	2.59	5.4	1.6
Ga_4As_4	Rhombic prism	C_i	2.54	5.1	0.4
	Bicapped octahedron	C_i	2.40	5.4	0.6
	Square antiprism	C_2	2.40	5.8	0.8
Ga_3As_3	Capped trigonal bipyramid	C_i	2.43	5.7	2.0
	Capped square pyramid	C_i	2.40	5.3	1.1
	Bicapped tetrahedron	C_i	2.30	5.3	0.9
	Trigonal antiprism	C_s	2.30	5.3	0.5

with that obtained in a recent CASSCF/MRSDCI calculation.²⁰ In addition, several three-dimensional configurations (within C_{2v} symmetry) were tried but found less stable.

The most stable trimer was found to be GaAs₂ in an isosceles triangle [Fig. 2(a)].

The bond lengths in these clusters span a range from 2.2 to 2.8 Å. The As–As bond length does not vary much from a middle value 2.5 Å. By contrast, the Ga–Ga bond length varies from 2.4 to 2.8 Å. The variation of Ga–As bond length is intermediate. This is consistent with the potential energy curves of the corresponding dimers plotted in Fig. 1.

IV. DISCUSSION

Recent experiments on Ga_xAs_y clusters have shown that the electronic affinity (EA) of gallium arsenide clusters oscillates with the number of atoms ($x + y$); the even-numbered clusters tend to have smaller EA and the odd-numbered clusters have larger EA.¹³ Similar even/odd oscillation is also observed in the ionization potentials (IP). The observed oscillation of EA and IP with cluster size strongly suggests that the even-numbered neutral gallium arsenide clusters be of significant HOMO–LUMO separations and therefore of singlet ground states (except for the dimer GaAs which is known to have a triplet ground state).

In Table II, it can clearly be seen that the present calculation give support for this interpretation.

The reactivity of GaAs clusters with ammonia has also been studied. It was found that the largest reactivity was obtained with equal numbers of Ga and As indicating that the atoms in GaAs clusters (of size 8 atoms and larger) may possibly be arranged in an alternating pattern with the Ga atoms losing electrons to the neighboring As atoms. The Lewis acid site thus formed at the cluster surface would allow a chemical bond between the ammonia molecule and the cluster surface.

This suggestion is also confirmed by the present calculation. The outermost sites are occupied by gallium atoms which are bound to neighboring arsenic atoms. Charges are transferred from the gallium atoms to the adjacent arsenic atoms. The tendency to alternating arrangements is clearly seen.

The close agreement between the calculated electronic properties and the experimental results shows that the electronic structure of Ga_xAs_y clusters can be conveniently described using the LDA theory. Ga_xAs_y clusters could therefore serve as very interesting model systems where it is possible to investigate how the details of the electronic structure influence the physical and chemical properties of the cluster. The LDA calculations are relatively straightforward to perform and very fast compared to other *ab initio* methods such as Hartree–Fock or CI. The simplicity of LDA allows relatively large clusters to be studied. At present, new LDA code is being developed employing a similar calculational technique as outlined in this paper,²¹ but specifically designed to execute on parallel computers. This new program

will allow the further detailed study and interpretation of various experiments on larger clusters.

V. CONCLUSION

The electronic structure of small GaAs clusters have been calculated using the local density approximation. Comparison with other theoretical calculations and experimental results for dimers show that the present approach provides very accurate results with a minimal computational effort. For larger GaAs clusters, the equilibrium geometries and electronic configuration has been calculated using total energy minimization. The results obtained is in agreement with experimental data.

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